11-21-00

A



Attorney's Docket No.: U 013054-6

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**Box Patent Application**
**Assistant Commissioner for Patents**
**Washington, D.C. 20231**

## NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of Inventors:

1. RAGHUNATH VITTHAL **CHAUDHARI**
2. CHANDRASHEKHAR VASANT **RODE**
3. RENGASWAMY **JAGANATHAN**
4. MANISHA MADHUKAR **TELKAR**
5. VILAS HARI **RANE**

***WARNING:*** *The Declaration must name all of the actual inventor(s).*

For (title):

NOBLE METAL CONTAINING HYDROGENATION CATALYST FOR SELECTIVE HYDROGENATION OF 1, 4 BUTYNEDIOL TO 1, 4 BUTENEDIOL, AND A PROCESS FOR THE PREPARATION THEREOF

1. **Type of Application**

This new application is for a(n) (check one applicable item below):

- ☑ Original (nonprovisional)
- ☐ Design
- ☐ Plant

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**CERTIFICATION UNDER 37 CFR 1.10**

I hereby certify that this New Application Transmittal and the documents referred to as enclosed therein are being deposited with the United States Postal Service on this date **NOVEMBER 20, 2000 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EL699732844US addressed to the: Assistant Commissioner of Patents, Washington, D.C. 20231**

**CONNIE YANNOTTI**
*(type or print name of person mailing paper)*

*(Signature of person mailing paper)*

***NOTE:*** ***Each paper or fee referred to as enclosed herein has the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 CFR 1.10(b).***

***WARNING:*** ***Certificate of mailing (first class) or facsimile transmission procedures of 37 CFR 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.***



EXPRESS MAIL LABEL
NO.: EL699732844US

*WARNING:* ***Do not*** *use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4) unless the International Application is being filed as a divisional, continuation or continuation-in-part application.*

*WARNING:* ***Do not*** *use this transmittal for the filing of a provisional application.*

## 2. Benefit of Prior U.S. Application(s) (35 U.S.C. 119(e), 120, or 121)

*NOTE: If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.*

*WARNING: If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

*WARNING: When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional* ***must*** *be filed prior to the Saturday, Sunday or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).*

☐ The new application being transmitted claims the benefit of prior U.S. application(s) and enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

*NOTE: If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.*

☐ Divisional.

☐ Continuation.

☐ Continuation-in-Part (C-I-P).

## 3. Papers Enclosed That Are Required For Filing Date Under 37 CFR 1.53 (Regular) or 37 CFR 1.153 (Design) Application

10 Pages of specification

2 Pages of claims

1 Pages of Abstract

_ Sheets of drawing

☐ formal

☐ informal

*WARNING:* ***DO NOT*** *submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. Comments on proposed new 37 CFR 1.84. Notice of March 9, 1988 (1990 O.G. 57-62).*

*NOTE: "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match*

*the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (⅝ inch) down from the top of the page." 37 C.F.R. 1.84(c).*

*(complete the following, if applicable)*

☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)". 37 C.F.R. 1.84(b).

**4. Additional papers enclosed**

☐ Preliminary Amendment

☐ Information Disclosure Statement (37 CFR 1.98)

☐ Form PTO-1449

☐ Citations

☐ Declaration of Biological Deposit

☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.

☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative

☐ Special Comments

☐ Other

**5. Declaration or oath**

☐ Enclosed

executed by *(check **all** applicable boxes)*

☐ inventors.

☐ legal representative of inventors. 37 CFR 1.42 or 1.43

☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.

☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. *See item 13 below for fee.*

☑ Not Enclosed.

***WARNING:*** *Where the filing is a completion in the U.S. of an International Application but where a declaration is not available or where the completion of the U.S. application contains subject matter in addition to the International Application the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.*

☑ Application is made by a person authorized under 37 CFR 1.41(c) on behalf of *all the above named inventors.* (The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently).

*NOTE: It is important that all the correct inventor(s) are named for filing under 37 CFR 1.41(c) and 1.53(b).*

☐ Showing that the filing is authorized. *(Not required unless called into question. 37 CFR 1.41(d).)*

**6. Inventorship Statement**

***WARNING:*** *If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.*

The inventorship for all the claims in this application are:

☐ The same

☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

**7. Language**

*NOTE: An application including a signed oath or declaration may be filed in a language other than English. A verified English translation of the non-English language application and the processing fee of $130.00 required by 37 CFR 1.17(k) is required to be filed with the application or within such time as may be set by the Office. 37 CFR 1.52(d).*

*NOTE: A non-English oath or declaration in the form provided or approved by the PTO need not be translated. 37 CFR 1.69(b).*

☑ English

☐ non-English

☐ the attached translation is a verified translation. 37 CFR 1.52(d).

**8. Assignment**

☑ An assignment of the invention to COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

☑ will follow.

*NOTE: "If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).*

*WARNING: A newly executed "CERTIFICATE UNDER 37 CFR 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993. 1150 O.G. 62-64.*

**9. Certified Copy**

Certified copy of application

| Country | Appln. No. | Filed |
|---|---|---|

from which priority is claimed

☐ is attached.

☐ will follow.

*NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 CFR 1.55(a) and 1.63.*

*NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.*

**10. Fee Calculation (37 CFR 1.16)**

A. ☑ Regular Application

| Claims as Filed |
|---|

| Number Filed | | Number Extra | | Rate | Basic Fee 37 CFR 1.16(a) $710.00 |
|---|---|---|---|---|---|
| Total Claims (37 CFR 1.16(c)) | 11 - 20 = | 0 x $ | | 18.00 | |
| Independent Claims (37 CFR 1.16(b)) | 4 - 3 = | 1 x $ | | 80.00 | 80.00 |
| Multiple dependent claim(s), if any (37 CFR 1.16(d)) | | | + $ | 270.00 | |

☐ Amendment cancelling extra claims enclosed.

☐ Amendment deleting multiple-dependencies enclosed.

☐ Fee for extra claims is not being paid at this time.

*NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 CFR 1.16(d).*

Filing Fee Calculation $

B. ☐ Design application ($320.00 — 37 CFR 1.16(f))

Filing Fee Calculation $

C. ☐ Plant application ($490.00 — 37 CFR 1.16(g))

Filing Fee Calculation $

**11. Small Entity Statement(s)**

☐ Verified Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is(are) attached or has been filed.

Filing Fee Calculation (50% of **A**, **B** or **C** above) $

*NOTE: Any excess of the full fee paid will be refunded if a verified statement and a refund request are filed within 2 months of the date of timely payment of a full fee. 37 CFR 1.28(a).*

**12. Request for International-Type Search (37 CFR 1.104(d)) *(Complete, if applicable)***

☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

**13. Fee Payment Being Made At This Time**

☑ Not Enclosed

☑ No filing fee is to be paid at this time. *(This and the surcharge required by 37 CFR 1.16(e) can be paid subsequently.)*

☐ Enclosed

☐ basic filing fee $

☐ Recording assignment
($40.00; 37 CFR 1.21(h)) (See attached "COVER SHEET FOR ASSIGNMENT ACCOMPANYING NEW APPLICATION.")

☐ Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached.
($130.00; 37 CFR 1.47 and 1.17(h)) $

☐ For processing an application with a specification in a non-English language.
($130.00; 37 CFR 1.52(d) and 1.17(k)) $

☐ Processing and retention fee
($130.00; 37 CFR 1.53(d) and 1.21(l))

☐ Fee for international-type search report
($40.00; 37 CFR 1.21(e)). $

*NOTE: 37 CFR 1.21(l) establishes a fee for processing and retaining any application which is abandoned for failing to complete the application pursuant to 37 CFR 1.53(d) and this, as well as the changes to 37 CFR 1.53 and 1.78, indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid or the processing and retention fee of §1.21(l) must be paid within 1 year from notification under §53(d).*

Total fees enclosed $

**14. Method of Payment of Fees**

☐ Check in the amount of $

☐ Charge Account No. 12-0425 in the amount of $

A duplicate of this transmittal is attached.

*NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).*

**15. Authorization to Charge Additional Fees**

***WARNING:*** *If no fees are to be paid on filing, the following items should not be completed.*

***WARNING:*** *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.*

☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 12-0425.

☐ 37 CFR 1.16(a), (f) or (g) (filing fees)

☐ 37 CFR 1.16(b), (c) and (d) (presentation of extra claims)

*NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.*

☐ 37 CFR 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)

☐ 37 CFR 1.17 (application processing fees)

***WARNING:*** *While 37 CFR 1.17(a), (b), (c) and (d) deal with extensions of time under §1.136(a), this authorization should be made only with the knowledge that: "Submission of the appropriate extension fee under 37 C.F.R. 1.136(a) is to no avail unless a request or petition for extension is filed." (Emphasis added). Notice of November 5,1985 (1060 O.G. 27)*

☐ 37 CFR 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 CFR 1.311(b))

*NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b).*

*NOTE: 37 CFR 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application ... prior to paying, or at the time of paying, ... issue fee". From the wording of 37 CFR 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.*

16. **Instructions As To Overpayment**

☐ credit Account No. 12-0425

☐ refund

*Signature of Attorney*

Reg. No. 33,778

Tel. No. (212) 708-1935

Janet I. Cord
Ladas & Parry
26 West 61 Street
New York, NY 10023

☐ **Incorporation by reference of added pages**

*(Check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)*

☐ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added ___

☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added ___

☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added ___

☑ **Statement Where No Further Pages Added**

*(If no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item:)*

☑ This transmittal ends with this page.

# NOBLE METAL CONTAINING HYDROGENATION CATALYST FOR SELECTIVE HYDROGENATION OF 1, 4 BUTYNEDIOL TO 1, 4 BUTENEDIOL, AND A PROCESS FOR THE PREPARATION THEREOF

## Field of the invention

The present invention relates to a noble metal containing hydrogenation catalyst for the selective hydrogenation of 1, 4 butynediol to 1, 4 butenediol. The present invention also relates to a process for the preparation of the said catalyst. More particularly, the present invention relates to said hydrogenation catalyst for the selective preparation of 1, 4 butynediol to 1, 4 butenediol, and a process for the preparation of the said catalyst.

## Background of the invention

1, 4 butenediol is a useful intermediate in the production of pesticide, insecticide and vitamin $B_6$. Being an unsaturated diol it can be used in the synthesis of many organic products such as tetrahydrofuran, n-methyl pyrrolidione, γ-butyrolactone, etc. It is also used as an additive in the paper industry, as a stabiliser in resin manufacture, as a lubricant for bearing systems and in the synthesis of allyl phosphates.

Prior art discloses the use of a number of catalysts for the manufacture of 1, 4 butenediol by the hydrogenation of 1, 4 butynediol. Most of the prior art patents are based on a combination of palladium with one or more mixed compounds of copper, zinc, calcium, cadmium, lead, alumna, mercury, tellurium, gallium, etc. GB A 871804 describes the selective hydrogenation of acetylinic compound in a suspension method using a Pd catalyst which has been treated with the salt solutions of Zn, Cd, Hg, Ga, Th, In, or Ga. The process is carried out at milder conditions with 97 % selectivity for cis 1,2-butenediol and 3 % to the trans form. Moreover, use of organic amines have been suggested as promoters in the catalyst system.

US Patent 2, 681,938 discloses the use of a Lindlar catalyst (lead doped Pd catalyst), for the selective hydrogenation of acetylinic compounds. The drawback of this process is the use of additional amines such as pyridine to obtain good selectivity for 1, 4 butenediol.

German patent DE 1, 213, 839 describes a Pd catalyst doped with Zn salts and ammonia for the partial hydrogenation of acetylinic compounds. However, this catalyst suffers from the drawback of short lifetime due to poisoning.

German patent application DE A 2, 619, 660 describes the use of $Pd/Al_2O_3$ catalyst that has been treated with carbon monoxide for the hydrogenation of butynediol in an inert solvent. The disadvantage of this catalyst is that is treated with carbon monoxide gas which is highly toxic and difficult to handle.

US Patent 2, 961, 471 discloses a Raney nickel catalyst useful for the partial hydrogenation of 1, 4 butynediol. The catalyst of this process gives a low selectivity for 1, 4 butenediol. Another US Patent 2, 953, 604 describes a Pd containing charcoal and copper catalyst for the reduction of 1,4 butynediol to 1,4 butenediol with 81 % selectivity for 1,4 butenediol. However, this process results in the formation of a large number of side products and is therefore undesirable.

US Patent 4, 001, 344 discloses the use of palladium mixed with $\gamma$- $Al_2O_3$ along with both zinc and cadmium or either zinc or cadmium together with bismuth or tellurium for the preparation of 1,4 butenediol by the selective hydrogenation of 1, 4 butynediol. However, a large number of residues are formed (7.5 – 12%) which lowers the selectivity of 1,4 butenediol to 88 %.

US Patent Nos. 5, 521, 139 and 5, 278, 900 describes the use of a Pd containing catalyst for the hydrogenation of 1,4 butynediol to prepare 1,4 butenediol. The catalyst used is a fixed bed catalyst prepared by applying Pd and Pb or Pd and Cd successively by vapor deposition or sputtering to a metal gauze or a metal foil acting as a support. In this process also the selectivity obtained for cis 1,4 butenediol is 98 %. The disadvantage of this process is that a trans butenediol with residues are also obtained.

All the above catalysts for the hydrogenation of butynediol to butenediol suffer from disadvantages such as they contain more than two metals along with other promoters such as organic amines. Their preparation becomes cumbersome and all the reported catalysts do not give complete selectivity for the desired product 1, 4 butenediol. The formation of side products and residues have also been reported which affect the efficiency of the process and the recovery of pure 1,4 butenediol is difficult. Another disadvantage that prior art catalysts suffer from is short life due to fast deactivation.

It is therefore important to obtain and/or develop catalysts that overcome the disadvantages of prior art catalysts used in the hydrogenation of 1,4 butynediol to 1,4 butenediol enumerated above.

**Objects of the invention**

The main object of the invention is to provide a novel hydrogenation catalyst for the selective preparation of 1, 4 butenediol that comprises a noble metal, individually or in combination with nickel, on a suitable support without poisoning at very specific preparation conditions for the selective production of 1, 4 butenediol.

It is another object of the invention to provide a process for the preparation of such novel hydrogenation catalysts for the preparation of 1,4 butenediol.

It is another object of the invention to provide a novel hydrogenation catalyst for the preparation of 1,4 butenediol that results in 100 % conversion of the butynediol and 100 % selectivity at mild process conditions.

It is another object of the invention to provide a catalyst with high stability that can be recycled several times without loss of activity and selectivity.

It is another object of the invention to provide a process for the preparation of 1,4 butenediol using the hydrogenation catalyst of the invention.

It is another object of the invention is to provide a novel catalyst for the selective hydrogenation of 1, 4 butynediol to 1, 4 butenediol that comprises only platinum on a suitable support, without poisoning at very specific preparation conditions.

It is an object of the invention to provide a process for the preparation of 1, 4 butenediol from 1,4 butynediol using a novel hydrogenation catalyst resulting in 1,4 butenediol of high purity by mere separation of the catalyst.

**Summary of the invention**

Accordingly the present invention provides a hydrogenation catalyst of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal or zeolite, B is a noble metal selected from palladium and platinum, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 % with the proviso that when B is Pt, z = 0.

In one embodiment of the invention, B is Pd and z = 0.2 – 10 %.

The present invention also relates to a process for the preparation of a hydrogenation catalyst of the general formula AB(y)C(z) wherein A is a support

comprising of a salt of a Group II A metal or zeolite, B is a noble metal selected from palladium and platinum, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 % with the proviso that when B is Pt, z = 0, said process comprising:

i. dissolving a noble metal precursor in a mineral acid by stirring at a temperature in the range between 60°C to 120°C;
ii. diluting the above solution by adding water;
iii. adjusting the pH of the solution to the range of 8 – 12 by adding a base;
iv. adding a support to the above solution;
v. heating the mixture to a temperature in the range of 60°C to 120°C;
vi. reducing the above mixture using a conventional reducing agent;
vii. separating the catalyst formed by any conventional method;
viii. washing and drying the product to obtain the said catalyst.

In a further embodiment of the invention, the noble metal comprises of palladium and z = 0.2 to 15 %, the catalyst obtained at the end of step viii above is mixed with a solution of nickel in a basic medium having a pH in the range of 8 – 12, the mixture stirred for about 1 hour and the catalyst is separated by any conventional method. The catalyst is then dried at about 150°C up to 10 hours in static air, reduced at a temperature in the range of between 390 - 420°C for a time period in the range of between 5 – 12 hours in a flow of hydrogen, the reduced catalyst is then separated by any conventional method and washed and dried to obtain the final catalyst containing palladium and nickel.

In one embodiment of the invention, the noble metal source is a noble metal salt selected from the group consisting of acetate, bromide, and chloride and the source of nickel is a salt of nickel selected from the group consisting of acetate, carbonate, chloride and nitrate.

In another embodiment of the invention, the support is a Group II A metal salt selected from the group consisting of acetates, nitrates, chlorides and carbonates of magnesium, calcium and barium and the source of zeolite is $NH_4$-ZSM5.

In a further embodiment of the invention, the base used may be selected from the group consisting of sodium carbonate, potassium carbonate, potassium hydroxide, and sodium hydroxide.

In another embodiment of the invention, the reducing agent used is selected from the group consisting of hydrazine hydrate, hydrogen containing gas, and formaldehyde.

The present invention also relates to a process for the preparation of 1, 4 butenediol from 1, 4 butynediol said process comprising subjecting the 1,4 butynediol to hydrogenation by any conventional method characterised in that the catalyst used for the hydrogenation is of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal or zeolite, B is a noble metal selected from palladium and platinum, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 %.

In a further embodiment of the invention, the selectivity of the process at milder process conditions is 100 %.

The present invention also relates to the use of a novel hydrogenation catalyst of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal or zeolite, B is a noble metal, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 %, for the preparation of 1,4 butenediol.

**Detailed description of the invention**

The present invention achieves 100 % conversion of 1,4 butynediol with 100 % selectivity for cis 1,4 butenediol at mild process conditions. At higher temperatures, while 1, 4 butynediol is converted completely, the selectivity for cis 1, 4 butenediol is less, generally $\leq$ 90 %. The formation of side products such as acetals, $\gamma$ - hydroxybutaraldehyde, butanol at higher temperatures is also more pronounced.

The hydrogenation of 1,4 butynediol to 1,4 butenediol is carried out in an autoclave under stirring conditions in the presence of Pd or Pt containing catalyst suspended in a mixture of 1, 4 butynediol in water at 50°C and 350 psig of $H_2$ pressure. The mixture is made alkaline (pH = 8 – 10) by the addition of ammonia. Before pressurising the autoclave, it was ensured that there was no air in the autoclave. The hydrogenation is complete when the absorption of hydrogen is stopped or unchanged. After the reaction was complete, the reactor was cooled below ambient temperature and the contents were discharged and the reaction mixture analysed using a gas chromatograph.

The catalyst prepared as per the procedure described below in the examples can be reduced in a muffle furnace at 400°C in hydrogen flow for a time period ranging between 5 – 12 hours, preferably 7 hours.

In a feature of the invention, high purity 1, 4 butenediol can be simply obtained by the removal of the catalyst from the product stream.

The present invention is described below by way of examples. However, the following examples are illustrative and should not be construed as limiting the scope of the invention.

**Example 1**

**Preparation of 1 % Pd/$MgCO_3$ catalyst**

0.17 gms of palladium chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the palladium chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.02 gms of magnesium carbonate was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml), stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours.

**Example 2**

**Preparation of1 % Pd/$CaCO_3$ catalyst**

0.17 gms of palladium chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the platinum chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.12 gms of calcium carbonate was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml), stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours.

**Example 3**

**Recycling of 1 % Pd/$CaCO_3$ catalyst**

This example illustrates the recycling of 1% Pd/CaCO3 catalyst wherein the catalyst preparation was similar to the disclosure in Example 2 above. The

hydrogenation of 1, 4 butynediol was carried out by recycling the catalyst 10 times at 50°C and 350 psig $H_2$ pressure as described earlier.

**Example 4**

**Preparation of 1 % Pd/$BaCO_3$ catalyst**

0.16 gms of palladium chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the palladium chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.1 gms of barium carbonate was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml), stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours.

**Example 5**

**Preparation of 1% Pd/$NH_4$-ZSM5 catalyst**

0.17 gms of palladium chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the palladium chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.0 gms of $NH_4$-ZSM5 was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml), stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours.

**Example 6**

**Preparation of 10 % Ni- 1% Pd/$CaCO_3$ catalyst**

0.17 gms of palladium chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the platinum chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.12 gms of calcium carbonate was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml), stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours. The dried catalyst is then mixed

with a solution of nickel nitrate and stirred in basic medium (pH = 9 – 10) for 1 hour, dried at 150°C for 10 hours in static air and then reduced at 400°C for 7 hours in a flow of hydrogen.

**Example 7**

**Preparation of 1 % Pt/$MgCO_3$ catalyst**

0.16 gms of platinum chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the platinum chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.13 gms of magnesium carbonate was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml), stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours.

**Example 8**

**Preparation of1 % Pt/$CaCO_3$ catalyst**

0.17 gms of platinum chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the platinum chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.03 gms of calcium carbonate was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml), stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours.

**Example 9**

**Preparation of 1 % Pt/$BaCO_3$ catalyst**

0.16 gms of platinum chloride was dissolved in 4 ml of hydrochloric acid and stirred at 80°C till the platinum chloride was completely dissolved. The resultant solution was diluted by adding 50 ml of water and stirring for 2 hours, the pH being maintained between 9 – 10 by the addition of sodium hydroxide. To the diluted solution, 10.05 gms of barium carbonate was added and the mixture heated at 80°C for 1 hour. The mixture was then reduced by the addition of formaldehyde (3 ml),

stirred for 45 minutes, filtered and washed with water till the solution is alkaline free. The catalyst was then dried at 150°C for 10 hours.

**Example 10**

**Performance of palladium or palladium and nickel supported catalysts of the invention as prepared in Examples 1 – 6 above**

This example illustrates the performance of the palladium or palladium and nickel supported catalysts of the invention as prepared in Examples 1 – 6 above in the hydrogenation of 1,4 butynediol to 1, 4 butenediol.

| Example No. | Catalyst | Conversion of 1, 4 butynediol (%) | Selectivity to cis 1, 4 butenediol (%) | Reaction period (hours) |
|---|---|---|---|---|
| 1 | 1 % $Pd/MgCO_3$ | 100 | 99.8 | 2 |
| 2 | 1 % $Pd/CaCO_3$ | 100 | 98.2 | 1 |
| 3 | 1 % $Pd/CaCO_3$* | 100 | 98 | 68 |
| 4 | 1 % $Pd/BaCO_3$ | 100 | 100 | 2 |
| 5 | 1% $Pd/NH_4$-ZSM 5 | 100 | 100 | 4 |
| 6 | 10 % Ni- 1 % $Pd/CaCO_3$ | 100 | 100 | 4 |

*catalyst recycled for 10 times

**Example 11**

**Performance of platinum supported catalysts of the invention as prepared in Examples 7 – 9 above**

This example illustrates the performance of the platinum supported catalysts of the invention as prepared in Examples 7 – 9 above in the hydrogenation of 1,4 butynediol to 1, 4 butenediol.

| Example No. | Catalyst | Conversion of 1, 4 butynediol (%) | Selectivity to cis 1,4 butenediol (%) | Reaction period (hours) |
|---|---|---|---|---|
| 7 | 1 % $Pt/MgCO_3$ | 100 | 99.8 | 2 |
| 8 | 1 % $Pt/CaCO_3$ | 100 | 100 | 1 |
| 9 | 1 % $Pt/BaCO_3$ | 100 | 99.9 | 2.5 |

**Advantages of the invention**

1. The catalyst of the invention is useful for the selective hydrogenation of 1, 4 butynediol to 1, 4 butenediol without poisoning.
2. Substantially complete conversion of 1, 4 butynediol to 1, 4 butenediol with almost 100 % selectivity to cis 1, 4 butenediol is obtained at milder process conditions.
3. The separation of the product 1, 4 butenediol in pure form is achieved easily by the removal of the catalyst from the reaction mixture.
4. The catalyst of the invention is capable of recycling several times without loss of activity or selectivity. The turn over number also is good.

**We claim:**

1. A hydrogenation catalyst of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal or zeolite, B is a noble metal selected from Pt or Pd, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 %, with the proviso that when B is Pt, z = 0.
2. A process for the preparation of a hydrogenation catalyst of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal or zeolite, B is a noble metal selected from Pd or Pt, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 %, with the proviso that when B is Pt, z = 0, said process comprising:

i. dissolving a noble metal precursor in a mineral acid by stirring at a temperature in the range between 60°C to 120°C;
ii. diluting the above solution by adding water;
iii. adjusting the pH of the solution to the range of 8 – 12 by adding a base;
iv. adding a support to the above solution;
v. heating the mixture to a temperature in the range of 60°C to 120°C;
vi. reducing the above mixture using a conventional reducing agent;
vii. separating the catalyst formed by any conventional method;
viii. washing and drying the product to obtain the catalyst.

3. A process as claimed in claim 2 wherein the catalyst obtained at the end of step viii is mixed with a solution of nickel in a basic medium having a pH in the range of 8 – 12; stirred for about 1 hour; the catalyst formed is separated by any conventional method; dried at about 150°C up to 10 hours in static air; reduced at a temperature in the range of between 390 - 420°C for a time period in the range of between 5 – 12 hours in a flow of hydrogen; the product being separated, washed and dried to obtain the catalyst.
4. A process as claimed in claim 2 wherein the noble metal source is a salt of a noble metal selected from the group consisting of acetate, bromide, and chloride of and the source of nickel is a salt of nickel selected from the group consisting of acetate, carbonate, chloride and nitrate.
5. A process as claimed in claim 2 wherein the support is a salt of a Group II A metal selected from the group consisting of acetates, nitrates, chlorides and

carbonates of magnesium, calcium and barium and the source of zeolite is $NH_4$-ZSM5.

6. A process as claimed in claim 2 wherein the base used is selected from the group consisting of sodium carbonate, potassium carbonate, potassium hydroxide, and sodium hydroxide.
7. A process as claimed in claim 2 wherein the reducing agent used is selected from the group consisting of hydrazine hydrate, hydrogen containing gas, and formaldehyde.
8. A process as claimed in claim 2 wherein A is a support comprising of a salt of a Group II A metal, B is platinum and y = 0.2 to 10 %, said process comprising:

i. dissolving a platinum precursor in a mineral acid by stirring at a temperature in the range between 60°C to 120°C;
ii. diluting the above solution by adding water;
iii. adjusting the pH of the solution to the range of 8 – 12 by adding a base;
iv. adding a support to the above solution;
v. heating the mixture to a temperature in the range of 60°C to 120°C;
vi. reducing the above mixture using a conventional reducing agent;
vii. separating the catalyst formed by any conventional method;
viii. washing and drying the product to obtain the desired catalyst.

9. A process for the preparation of 1, 4 butenediol from 1, 4 butynediol said process comprising subjecting the 1,4 butynediol to hydrogenation by any conventional method characterised in that the catalyst used for the hydrogenation is of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal, B is a noble metal selected from Pd and Pt, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 % with the proviso that when B is Pt, z = 0.
10. A process as claimed in claim 8 wherein the selectivity of the process at milder process conditions is 100 %.
11. Use of a novel hydrogenation catalyst of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal or zeolite, B is a noble metal selected from Pd and Pt, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 % with the proviso that when B is Pt, z = 0, for the preparation of 1,4 butenediol from 1, 4 butynediol.

**ABSTRACT**

A hydrogenation catalyst of the general formula AB(y)C(z) wherein A is a support comprising of a salt of a Group II A metal or zeolite, B is a noble metal selected from Pt or Pd, y = 0.2 to 10 %, C is nickel and z = 0 to 15.0 %, with the proviso that when B is Pt, z = 0.